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# Catalytic wet air oxidation of succinic acid over Ru and Pt catalysts supported on Ce$_x$Zr$_{1-x}$O$_2$ mixed oxides

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### ABSTRACT

Different Ce$_x$Zr$_{1-x}$O$_2$ mixed oxides, prepared by co-precipitation and Ce$_x$Zr$_{1-x}$O$_2$-supported platinum and ruthenium catalysts, synthesised by impregnation, were investigated in the catalytic wet air oxidation (CWAO) of succinic acid at 190°C under 50 bar total pressure. The catalytic activity of these solids was demonstrated to be strongly influenced by the Ce content in the Ce$_x$Zr$_{1-x}$O$_2$ support. The higher the Ce content in the mixed oxide support, the higher the succinic acid removal rate. The ruthenium catalysts exhibited the best performances in terms of succinic conversion at a given time of reaction; but, when the activity was expressed per mole of metal, the platinum catalysts were observed to perform better (435 mol$_{acid}$ h$^{-1}$ mol$_{Pt}$$^{-1}$). Upon recycling reactions, the Ce$_{0.9}$Zr$_{0.1}$O$_2$ support and the 0.5 wt% Ru/Ce$_{0.9}$Zr$_{0.1}$O$_2$ catalyst maintained some good performances even though the conversion of succinic acid gradually decreased. It was demonstrated that the leaching of the metallic phase, the formation of carbonaceous deposits on the catalyst surface and the decrease of the specific surface area did not play a major role in the deactivation, which was more likely related to modifications of the chemical state of the active phase. Finally, the reaction was shown to be +0.1 order with respect to succinic acid and +0.4 order with respect to oxygen, indicating some major changes in the reaction kinetics and mechanism of the reaction over such catalysts containing ceria.

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## 1. Introduction

Industries often generate large quantities of wastewaters with high organic loads and high toxicity. Such effluents are hardly decontaminated using biological treatments, the most common technology for wastewater treatment. Moreover, if directly discharged into the environment, such wastewaters would represent a serious environmental issue. The wet air oxidation (WAO) is an effective technology to eliminate toxic, hazardous and highly concentrated organic compounds to $CO_2$, $H_2O$ and other innocuous end products, under high temperature (120–320°C) and high pressure (0.5–20 MPa), using oxygen or air as the oxidant [1,2]. The application of such technology for treating industrial wastewaters might be limited because of these operating conditions and the related high investment costs. The addition of a catalyst may efficiently decrease the operating conditions which are required, increase the

oxidation rate of the organic compounds and shorten the reaction time. Homogenous catalysts ($Cu^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $Co^{2+}$, . . .) were used first, and demonstrated some good performances in the catalytic wet air oxidation (CWAO) of organic compounds, but an additional step is then required to remove metal ions in the effluents [3–5]. Compared to homogenous catalysts, heterogeneous catalysts have received much more attention since they do not require any further separation step. Noble metals (Pt, Ru, Pd, Au, . . .), transition metal oxides and carbon materials have been widely investigated in the CWAO of organic compounds, such as phenols, carboxylic acids, N-containing compounds [6–9]. However, a deactivation of heterogeneous catalysts is sometimes observed in the CWAO reaction [10–12], because of (1) the leaching of the active phases, (2) the deposition of carbonaceous species which limit the accessibility of the reactants to the active phases, or (3) the oxidation of the metallic phases which become less active. Therefore, the development of active and stable heterogeneous catalysts has gained a great attention.

Noble metal catalysts, especial the Ru and Pt catalysts, have shown the best activity and chemical stability in the CWAO of different model compounds as well as industrial wastewaters [13–19].

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Metal oxides ($TiO_2$, $ZrO_2$, $CeO_2$, $SiO_2$, $Al_2O_3$, . . .) and carbon materials are often used as supports during the CWAO process. Among them, $CeO_2$ has been paid a lot of attention, due to its resisting of both acidic and basic media, and maintaining of good chemical and thermal stability whatever the reaction conditions encountered [13]. Especially, $CeO_2$ was determined to enhance oxygen activation properties, which were shown to be beneficial for a number of reactions, such as three-way catalysis, methane reforming, water–gas shift and CWAO [20–24]. Compared to pure $CeO_2$, the $Ce_xZr_{1-x}O_2$ mixed oxides were shown to be more resistant towards sintering at high temperature and to further promote the oxygen activation upon the CWAO [18,23]. In addition, a synergy between the $Ce_xZr_{1-x}O_2$ mixed oxides and the active phase of the catalyst was evidenced, due to their good chemical stability and the oxygen transfer from liquid phase to the active sites on the catalyst surface [23].

In this article, the $Ce_xZr_{1-x}O_2$ mixed oxides were synthesized by co-precipitation, and the $Ce_xZr_{1-x}O_2$-based Ru and Pt catalysts were prepared by impregnation. The $Ru/Ce_xZr_{1-x}O_2$ and $Pt/Ce_xZr_{1-x}O_2$ catalysts were investigated in the CWAO of succinic acid at high reaction temperature, and the catalytic performance was compared between the prepared $Ce_xZr_{1-x}O_2$-based catalysts and other metal-oxide-based Pt and Ru catalysts, to understand the effect of the $Ce_xZr_{1-x}O_2$ mixed oxide on the activity of the Ru and Pt catalysts. Moreover, the stability of the $Ru/Ce_xZr_{1-x}O_2$ catalysts was assessed upon recycling experiments in a batch reactor to get better insights on the performances of the $Ce_xZr_{1-x}O_2$-based Ru catalysts in the CWAO of succinic acid. In addition, the reaction kinetics were studied in detail in the CWAO of succinic acid over the $Ru/Ce_{0.9}Zr_{0.1}O_2$ catalyst to evaluate more detailed information on the reaction mechanism and the impact of the ceria-containing mixed oxides.

## 2. Experimental

### 2.1. Catalyst preparation

$Ce_xZr_{1-x}O_2$ mixed oxides were prepared by co-precipitation. Aqueous solutions of $Ce(NO_3)_3$ and $ZrOCl_2$ were added dropwise in an ammonia solution under continuous and vigorous stirring. Precipitation occurred almost instantaneously and ammonia was further added to the solution to reach an alkaline pH of 10. The mixture was aged at ca. 80°C for 8 h while the pH was maintained at ca. 10. Afterwards, the precipitate was sequentially washed with distilled water and ethanol, and finally dried at ca. 100°C overnight. The received solid was grinded and subsequently calcined at 500°C for 6 h under flowing air (60 L h$^{-1}$) to get the $Ce_xZr_{1-x}O_2$ mixed oxides. The preparation route was presented in detail in a previous article [24].

The supported Pt and Ru catalysts were prepared via wet impregnation using $Pt(NH_3)_4(NO_3)_2$ and $Ru(NO)(NO_3)_3$ as metal precursors, respectively. The $Ce_xZr_{1-x}O_2$ mixed oxides were added to the aqueous solution of the Pt and Ru salts at room temperature, and then dried in an evaporation oven at 50°C for 3 h. The received Pt and Ru solids were respectively reduced at 210°C and 300°C for 2 h under flowing $H_2$ (60 L h$^{-1}$) to obtain the 0.5 wt% $Pt/Ce_xZr_{1-x}O_2$ and 0.5 wt% $Ru/Ce_xZr_{1-x}O_2$ catalysts.

### 2.2. Catalysts characterization

All samples were previously characterized by XRD and nitrogen adsorption at 77 K [24].

In addition, the geometric surface area developed by the crystallite could be calculated from the average crystallite size ($d$) deduced from the XRD measurements as follows, assuming spherical crystallites:

$$S_{crystallite} = \frac{60000}{\rho \times d}$$

where $S_{crystallite}$ is the geometric surface area developed by the crystallite (m$^2$ g$^{-1}$); $\rho$ is the density of the mixed oxides (g cm$^{-3}$), estimated from the linear combination of the density of pure ceria (7.13 g cm$^{-3}$) and pure zirconia (5.89 g cm$^{-3}$) based on the mass composition of the mixed oxide ($Ce_xZr_{1-x}O_2$); and $d$ is the crystallite size (nm).

Furthermore, the used catalysts were characterized by using both infrared (Bruker Vector 22 FT-IR, DTGS detector) and a total organic carbon analyser (Shimadzu TOC 5050A). FT-IR analysis was performed to observe the possible formation of carbonaceous deposits on the catalytic surface upon reaction. Spectra were recorded in the 4000–400 cm$^{-1}$ range, with a resolution of 2 cm$^{-1}$ after accumulating 100 scans. To prepare the pellets, ca. 2 mg of the sample was mixed with ca. 198 mg of KBr. TOC measurements on the catalysts after reaction were performed on a solid sample unit (SSM-5000) connected to a Shimadzu 5050 TOC analyser. The total carbon (TC) and inorganic carbon (IC) contents were measured independently. TC was measured after catalytic combustion at 900°C; while IC was measured after acidification of the sample with $H_3PO_4$ and heating at 200°C. In both cases, $CO_2$ was quantified by infrared. All analysis were performed in triplicate and over ca. 0.7 g samples to test the reproducibility of the measurement and minimize the possible impact of weighing errors or errors due to the heterogeneous distribution of the carbon over the sample. The maximum deviation in our case was less than ±5%.

### 2.3. CWAO experiments

CWAO of succinic acid was carried out in a 300 mL autoclave equipped with a magnetically driven stirrer to avoid any mass transfer limitation. A given mass of catalyst (2 or 5 g L$^{-1}$) and 150 mL succinic acid solution (1–5 g L$^{-1}$) were used for each experiment. After purging at least three times with Ar to remove any trace of oxygen, the reactor was heated to the desired reaction temperature (150–190°C), and either synthetic air (20 vol.% $O_2$ in $N_2$) or pure oxygen was introduced in the reactor to reach 50 bar total pressure. The stirrer was then switched on again. This time was considered as zero time for the reaction. Samples were periodically withdrawn from the reactor to monitor the reaction. The evolution of concentration of the reactant and reaction intermediates was followed using high performance liquid chromatography (HPLC). The HPLC system was equipped with a CarboSep Coregel-87H3 column and a UV-detector set at 210 nm. The mobile phase was an aqueous sulphuric acid solution (0.005 M) and the flow rate was set at 0.5 mL min$^{-1}$.

Moreover, to evaluate the degree of mineralization of the organic compounds in the effluent, a Shimadzu TOC-VCSH TOC analyser was used to measure the non-purgeable organic carbon (NPOC) in the liquid samples. After acidification down to pH 2 for the elimination of the inorganic carbon and the purgeable organic carbon, the sample was burnt in the catalytic oven heated at 680°C and the $CO_2$ produced was quantified with a non-dispersive infrared (NDIR) detector.

Finally, the reaction mixture at the end of the reaction was further analysed by ICP-OES to check for any leaching of the catalyst's constituents (i.e. Pt, Ru, Ce and Zr) upon the CWAO. The detection limit for Pt and Zr was 0.05 mg L$^{-1}$, while the detection limit for Ce and Ru was 0.1 mg L$^{-1}$.

**Table 1**
$Ce_xZr_{1-x}O_2$ mixed oxide characteristics.

| Samples[*] | BET surface area[**] ($m^2 g^{-1}$) | Crystallite size, $d$[**] (nm) | Crystallite geometric (external) surface area, $S_{crystallite}$[***] ($m^2 g^{-1}$) |
|---|---|---|---|
| $CeO_2$ | 101 | 8.7 | 97 |
| $Ce_{0.9}Zr_{0.1}O_2$ | 102 | 8.6 | 99 |
| $Ce_{0.75}Zr_{0.25}O_2$ | 148 | 5.1 | 171 |
| $Ce_{0.65}Zr_{0.35}O_2$ | 131 | 5.5 | 161 |
| $Ce_{0.5}Zr_{0.5}O_2$ | 151 | 4.4 | 206 |
| $Ce_{0.16}Zr_{0.84}O_2$ | 152 | 5.3 | 184 |

[*] Atomic composition.
[**] From Ref. [24].
[***] See Section 2.2

## 3. Results and discussion

### 3.1. Characterization

The main characteristics of the samples used in this study (surface area, lattice parameter, crystallite size, crystal composition, chemical composition, $pH_{ZPC}$) were already reported in a previous article [24]. All the mixed oxides appeared to be solid solutions, except the $Ce_{0.65}Zr_{0.35}O_2$ which appeared to consist in a crystalline cerium-rich phase and a separate XRD-invisible zirconium-rich phase.

In addition, the geometric surface area (external surface) of the crystallite for the $Ce_xZr_{1-x}O_2$ mixed oxides was calculated. The results are collected in Table 1. It appeared that the geometric surface area increased as the average crystallite size decreased upon introduction of zirconium in the ceria lattice. Furthermore, by comparing with the specific surface area measured by nitrogen adsorption at 77 K and the external surface area, we observed that (1) in the 0.9–1 cerium content range, the two values are identical, indicating that the oxide particles are single crystals and (2) at lower Ce content the external surface area is slightly higher than the specific area, indicating that the oxide particles are somehow bigger than the crystallite, i.e. that the mixed oxide particles are most probably polycrystalline.

### 3.2. CWAO of succinic acid over the bare $Ce_xZr_{1-x}O_2$ supports

In the absence of any catalyst, succinic acid was demonstrated to be thermally stable and no succinic acid removal was evidenced even after 360 min reaction (not shown).

Fig. 1 shows the evolution of the succinic acid concentration upon CWAO over the different $Ce_xZr_{1-x}O_2$ mixed oxides at 190 °C and under 50 bar total pressure (ca. 7 bar oxygen partial pressure, i.e. about 0.3 $g_{O2}$ $L^{-1}$ in the aqueous phase). The bare $Ce_xZr_{1-x}O_2$ mixed oxides exhibited 'good' catalytic performances in the CWAO of succinic acid, in comparison with the bare $ZrO_2$ and $TiO_2$ supports [25]. After 360 min reaction, 100% succinic acid conversion was achieved in all cases, except for $Ce_{0.16}Zr_{0.84}O_2$.

Noteworthy, the conversion of succinic acid was significantly and quite linearly dependent on the Ce content in the $Ce_xZr_{1-x}O_2$ mixed oxides. The higher the Ce content, the higher the conversion of succinic acid after 60 min reaction. For example, when the Ce content increased from 0.16 to 1 at.%, the succinic acid conversion varied from 23 to 82% after 180 min reaction. Similarly, the initial reaction rate, expressed per gram of catalyst, varied from 1.4 to 5.8 $mmol_{acid}$ $h^{-1}$ $g^{-1}$ as the cerium content increased from 16 to 100 at.% (Table 2). The pure $CeO_2$ and $Ce_{0.9}Zr_{0.1}O_2$ oxides showed the highest performances in the CWAO of succinic acid under the applied reaction conditions.

The evolution of the TOC content in the reaction mixture upon reaction was also monitored. It was found that succinic acid was
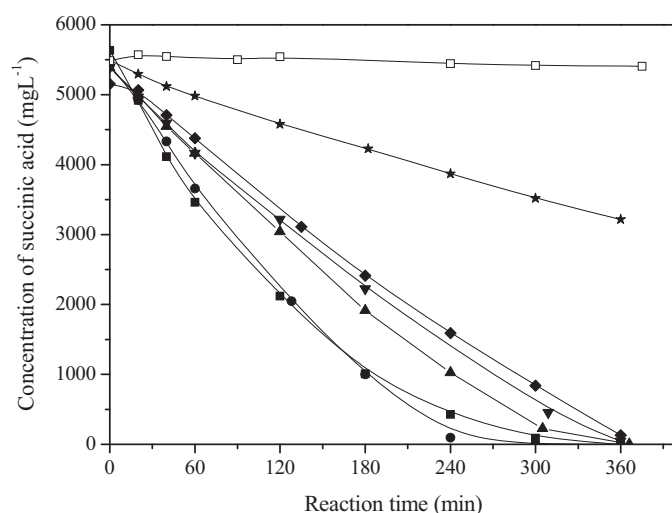


**Fig. 1.** WAO (□) and CWAO of succinic acid (5 g $L^{-1}$) over the $Ce_xZr_{1-x}O_2$ mixed oxides (0.5 g catalyst) at 190 °C under 50 bar total pressure. Impact of the support composition [$x = 1$ (■); 0.9 (●); 0.75 (▲); 0.65 (▼); 0.5 (◆); 016 (★)].

not completely mineralized to $CO_2$ and $H_2O$ after 360 min, even though 100% succinic acid removal was achieved (Table 2).

From the HPLC analysis, the main reaction intermediates were identified to be acetic and acrylic acids. The evolution of the concentrations of acetic and acrylic acids upon CWAO of succinic acid over $Ce_{0.9}Zr_{0.1}O_2$ is presented in Fig. 2. Acrylic acid was transiently produced at the beginning of the reaction and then was rapidly removed from the reaction mixture upon further reaction. On the opposite, acetic acid was observed (1) to be produced at a much constant rate at the beginning of the reaction, (2) to accumulate in the liquid phase until complete conversion of succinic acid (competitive adsorption), (3) to be oxidized at a much lower rate compared to succinic acid (refractory) and (4) to remain in the reaction mixture even after 360 min reaction (incomplete mineralization of succinic acid). This observation indicated that the $Ce_xZr_{1-x}O_2$ mixed oxides were not highly efficient in the removal of acetic acid under the applied reaction conditions. Indeed, acetic acid was shown to be refractory towards oxidation and higher reaction temperatures were required to achieve full acetic acid conversion, even in the presence of noble metal catalysts [25].
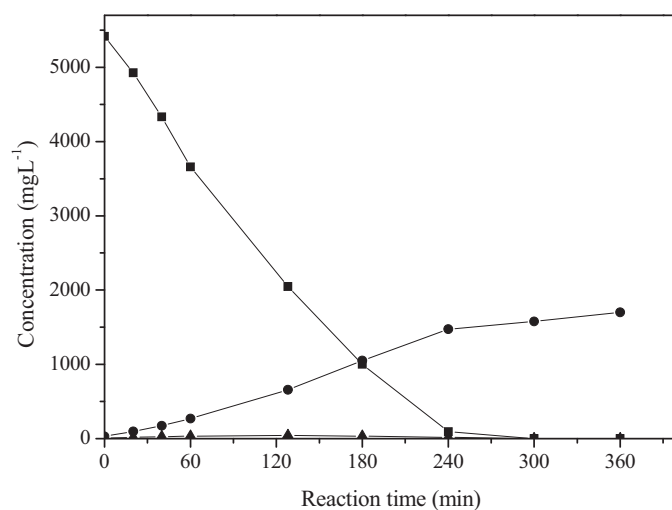


**Fig. 2.** Concentration profiles of reactant and products in solution upon CWAO of succinic acid (5 g $L^{-1}$) over the $Ce_xZr_{1-x}O_2$ supports (0.5 g) at 190 °C under 50 bar total pressure [succinic acid (■); acetic acid (●); acrylic acid (▲)].

**Table 2**
CWAO of succinic acid over bare $Ce_xZr_{1-x}O_2$ mixed oxides at 190°C under 50 bar total pressure (5 g L$^{-1}$ succinic acid, 0.5 g catalyst).

| Samples[*] | Initial reaction rate[**] (mmol$_{acid}$ h$^{-1}$ g$^{-1}$) | Succinic acid conversion after 40 min reaction (%) | TOC abatement after 40 min reaction (%) | Succinic acid conversion after 360 min reaction (%) | TOC abatement after 360 min reaction (%) | Carbon adsorbed on the catalyst (wt%) |
|---|---|---|---|---|---|---|
| $CeO_2$ | 5.8 | 27 | 25 | 100 | 65 | 1.0 |
| $Ce_{0.9}Zr_{0.1}O_2$ | 4.1 | 20 | 16 | 100 | 67 | 1.0 |
| $Ce_{0.75}Zr_{0.25}O_2$ | 3.2 | 17 | 15 | 100 | 61 | 1.0 |
| $Ce_{0.65}Zr_{0.35}O_2$ | 3.0 | 15 | 14 | 99 | 66 | 1.5 |
| $Ce_{0.5}Zr_{0.5}O_2$ | 2.6 | 12 | 11 | 98 | 67 | 1.9 |
| $Ce_{0.16}Zr_{0.84}O_2$ | 1.4 | 7 | 6 | 42 | 32 | 3.1 |

[*] Atomic composition.
[**] Calculated from the data acquired within the first 40 min of reaction.

Moreover, the TOC values measured directly with the Shimadzu analyser ($TOC_{meas}$) could be compared to the TOC values we could calculate from the concentrations of the different reaction intermediates detected by HPLC ($TOC_{cal}$). The evolution of two TOC values ($TOC_{meas}$ and $TOC_{cal}$) upon CWAO of succinic acid over $Ce_{0.9}Zr_{0.1}O_2$ is shown in Fig. 3. An excellent match between the values was clearly observed, indicating that (1) the mass balance was complete and (2) all the reaction intermediates in the liquid phase had been properly identified and quantified.

Furthermore, upon CWAO of organic compounds, carbonaceous deposits may form on the catalyst surface [9,16,18]. The adsorption of organic residues might be responsible for the degradation of the catalyst efficiency, as earlier reported in the CWAO of phenol over different catalysts. In our study, to differentiate between the adsorption on the catalyst surface and the real conversion of succinic acid and to evaluate the effective catalytic performances, the carbonaceous deposit on the different $Ce_xZr_{1-x}O_2$ mixed oxides after reaction was quantified by measuring the TOC content on the solid at the end of the reaction. It was observed that the amount of carbon deposited on the catalyst surface after reaction was very low (ca. 1 wt%), corresponding to less than 2 wt% of the initial carbon introduced in the reactor as succinic acid. In addition, the succinic acid adsorption on the mixed oxides was evaluated before the introduction of air pressure in the reactor, i.e. just before zero time. Actually, almost no adsorption of succinic acid was ever observed, except for $Ce_{0.5}Zr_{0.5}O_2$. These results indicated that succinic acid and the reaction intermediates did not strongly adsorb on the mixed oxide surface upon reaction. Consequently, the removal of succinic acid from the aqueous solution could be unambiguously attributed to an effective mineralization of succinic acid over highly active $Ce_xZr_{1-x}O_2$ mixed oxides.

Finally, the oxygen transfer from the solution up to the active sites on the catalyst surface was earlier reported to be kinetically limiting upon CWAO of organic compounds [13,24]. It was also reported that, depending on the composition of the $Ce_xZr_{1-x}O_2$ solid solutions, oxygen vacancies might be present on the oxide surface and promote the formation of highly reactive surface oxygen species, such as peroxides and/or superoxides, upon exposure to gaseous oxygen [23,24]. As mentioned before and exemplified in Fig. 3 and Table 2, it was observed in this study that the catalytic activity of the bare $Ce_xZr_{1-x}O_2$ mixed oxides correlated quite well with the Ce content. The excellent performances of the $Ce_xZr_{1-x}O_2$ mixed oxides in the CWAO of succinic acid could be clearly related (1) to the higher ability of the mixed oxides to activate the dissolved oxygen molecule as well as (2) to the higher mobility of oxygen at the surface of such oxides, facilitating the transfer of oxygen up to the active sites. These results constituted a good proof of concept concerning the ability of such bare mixed oxides to efficiently activate the oxygen molecules dissolved in the aqueous phase and to promote the CWAO oxidation of organic compounds whenever the temperature is high enough to promote the oxygen activation on the oxide surface. $Ce_xZr_{1-x}O_2$ mixed oxides would clearly offer an additional activation pathway for oxygen and promote the activity. Indeed, such effect was also partly observed in the CWAO of formic acid at low temperature [24].

### 3.3. CWAO of succinic acid over 0.5 wt% Pt/Ce$_x$Zr$_{1-x}$O$_2$ catalysts

Fig. 4 shows the evolution of the succinic acid concentration upon CWAO over the different 0.5 wt% Pt/Ce$_x$Zr$_{1-x}$O$_2$ catalysts at 190°C under 50 bar total pressure. All platinum catalysts appeared to be highly active in the conversion of succinic acid (although the platinum loading was very low) and to perform much better than the bare supports. The 0.5 wt% Pt/CeO$_2$ and 0.5 wt% Pt/Ce$_{0.9}$Zr$_{0.1}$O$_2$ catalysts showed the best activity. After only 180 min reaction, 100% succinic acid conversion was achieved.

However, although the platinum content was about the same for all catalysts (ca. 0.4 wt%), the catalyst performances appeared to be markedly different depending on the supports. The composition of the mixed oxide support also influenced the overall performances of the Pt catalysts: the higher the Ce content in the $Ce_xZr_{1-x}O_2$ support, the higher the succinic acid conversion. For the 0.5 wt% Pt/CeO$_2$ and 0.5 wt% Pt/Ce$_{0.16}$Zr$_{0.84}$O$_2$ catalysts, the conversion of succinic acid after 180 min was 100% and 36% and the initial reaction rate was 225 and 52 mol$_{acid}$ h$^{-1}$ mol$_{Pt}$$^{-1}$, respectively; although the 0.5 wt% Pt/Ce$_{0.16}$Zr$_{0.84}$O$_2$ catalyst had much higher surface area than 0.5 wt% Pt/CeO$_2$ catalyst.

Moreover, whatever the Pt catalyst, the mineralization of succinic acid was never complete (ca. 70% maximum) and acetic acid
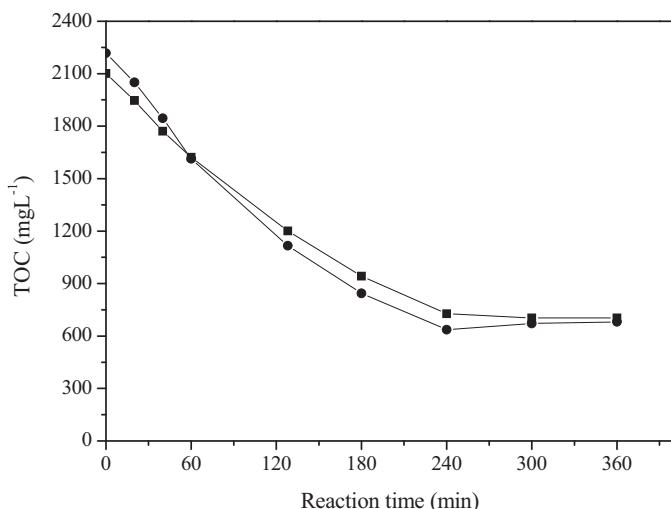


**Fig. 3.** Comparison of the evolution of the TOC values either directly measured with the TOC analyser ($TOC_{meas}$) or calculated from the HPLC analysis data ($TOC_{cal}$), upon CWAO of succinic acid at 190°C under 50 bar total pressure in the presence of $Ce_{0.9}Zr_{0.1}O_2$ [$TOC_{meas}$ (■); $TOC_{cal}$ (●)].

**Table 3**
CWAO of succinic acid over 0.5 wt% $Pt/Ce_xZr_{1-x}O_2$ catalysts at 190°C under 50 bar total pressure (5 g L$^{-1}$ succinic acid, 0.5 g catalyst).

| Samples[*] | Pt loading(wt%)[**] | Initial reaction rate (mol$_{acid}$ h$^{-1}$ mol$_{Pt}$$^{-1}$)[***] | Succinic acid conversion after 40 min reaction (%) | TOC abatement after 40 min reaction (%) | Succinic acid conversion after 360 min reaction (%) | TOC abatement after 360 min reaction (%) | Ce leaching (mg L$^{-1}$) | Carbon adsorbed on the catalysts (wt%) |
|---|---|---|---|---|---|---|---|---|
| $Pt/CeO_2$ | 0.40 | 435 | 27 | 18 | 100 | 60 | 0.74 | 1.0 |
| $Pt/Ce_{0.9}Zr_{0.1}O_2$ | 0.39 | 387 | 34 | 25 | 100 | 65 | – | 1.1 |
| $Pt/Ce_{0.75}Zr_{0.25}O_2$ | 0.40 | 231 | 22 | 17 | 100 | 68 | 0.32 | 1.7 |
| $Pt/Ce_{0.65}Zr_{0.35}O_2$ | 0.29 | 292 | 20 | 12 | 100 | 68 | – | 1.3 |
| $Pt/Ce_{0.5}Zr_{0.5}O_2$ | 0.29 | 262 | 16 | 9 | 93 | 60 | 0.10 | 3.3 |
| $Pt/Ce_{0.16}Zr_{0.84}O_2$ | 0.34 | 101 | 8 | 10 | 62 | 50 | 0.96 | 2.9 |

[*] Atomic composition.
[**] Determined by ICP-OES.
[***] Calculated from the data acquired within the first 40 min of reaction

appeared as the unique refractory product at the end of the reaction. All these data are summarized in Table 3.

Furthermore, the presence of carbonaceous deposits on the catalyst surface at the end of the reaction is shown in Table 3. The maximum carbon content in the solid catalyst after reaction was shown to be 3.3 wt% in the case of the $Pt/Ce_{0.5}Zr_{0.5}O_2$ catalyst. These values appeared to be quite low compared to the total amount of carbon initially introduced in the reactor as succinic acid. However, considering the carbon content on the solid, the specific surface area of the oxide and the lattice parameter of the oxide and based on a simple geometric model, we could calculate that such carbon deposit would approximately represent up to a monolayer of carbon onto the oxide surface.

In addition, chemical analysis (ICP-OES) was systematically performed on the reaction mixture at the end of the reaction to check for any leaching of the catalyst constituents. Neither Pt nor Zr was ever detected. However, trace amounts of Ce were almost systematically detected in the aqueous solutions after 360–480 min reaction. Still, these concentrations accounted for less than 0.1% of the initial Ce introduced in the reactor (0.5 g catalyst). Furthermore, no leaching at all was evidenced for the 0.5 wt% $Pt/Ce_{0.9}Zr_{0.1}O_2$ catalyst which appeared to be the most active and stable catalyst in the CWAO of succinic acid under the applied reaction conditions.

Finally, this result could be compared to some earlier results already reported in the literature. For example, Perkas et al. [25] reported on (1) the preparation under ultrasounds of platinum-based catalysts supported on mesoporous oxides (e.g. 2.1 wt% $Pt/TiO_2$ [MSP]) and (2) the evaluation of these catalysts in the CWAO of succinic acid under the same operating conditions (190°C,

50 bar total pressure). These catalysts were the best performing up to date and the authors observed that the nature of the support, the deposition method employed for the introduction of platinum on the support and the nature of the pre-treatment of the catalyst before reaction had a strong impact on the catalyst performances. Although the platinum loading was higher in the case of the solids prepared by Perkas et al. compared to the 0.5 wt.$Pt/Ce_xZr_{1-x}O_2$ catalysts developed in this study, we could calculate that the best 0.5 wt% $Pt/Ce_xZr_{1-x}O_2$ catalysts performed up to ca. 27 times better than the catalysts developed by Perkas et al. when the initial reaction rate was expressed per mole of platinum (435 vs 16 mol$_{acid}$ h$^{-1}$ mol$_{Pt}$$^{-1}$). These results indicated that the $Ce_xZr_{1-x}O_2$ mixed oxide supports played an important role in the catalytic performances of the Pt catalysts.

### 3.4. CWAO of succinic acid over the 0.5 wt% $Ru/Ce_xZr_{1-x}O_2$ catalysts

Fig. 5 shows the evolution of the succinic acid concentration upon CWAO over the $Ce_xZr_{1-x}O_2$-based Ru catalysts at 190°C under 50 bar total pressure. Looking at the succinic acid conversion, the 0.5 wt% $Ru/Ce_xZr_{1-x}O_2$ catalysts exhibited significantly higher activities compared to the 0.5 wt% $Pt/Ce_xZr_{1-x}O_2$ catalysts. After only 120 min reaction, ca. 100% succinic acid conversion was achieved, except for the 0.5 wt% $Pt/Ce_{0.5}Zr_{0.5}O_2$ and 0.5 wt% $Pt/Ce_{0.16}Zr_{0.84}O_2$ catalysts. The higher performances of the Ru catalysts in the complete mineralization of succinic acid compared to
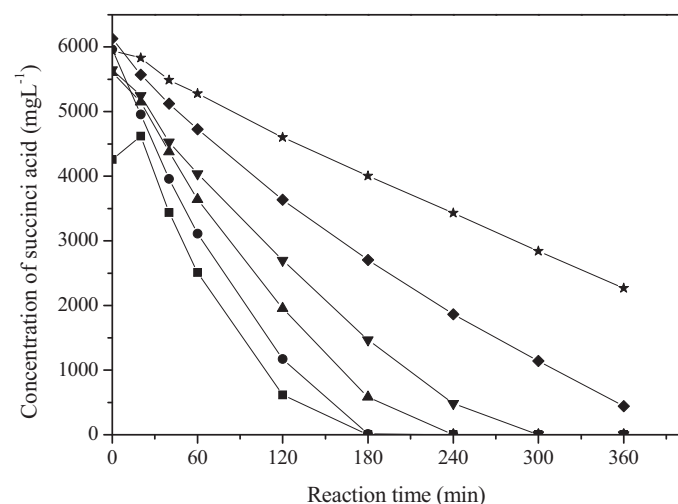


**Fig. 4.** CWAO of succinic acid (5 g L$^{-1}$) over the 0.5 wt% $Pt/Ce_xZr_{1-x}O_2$ catalysts (0.5 g catalyst) at 190°C under 50 bar total pressure. Influence of the support composition [x = 1 (■); 0.9 (●); 0.75 (▲); 0.65 (▼); 0.5 (◆); 0.16 (★)].
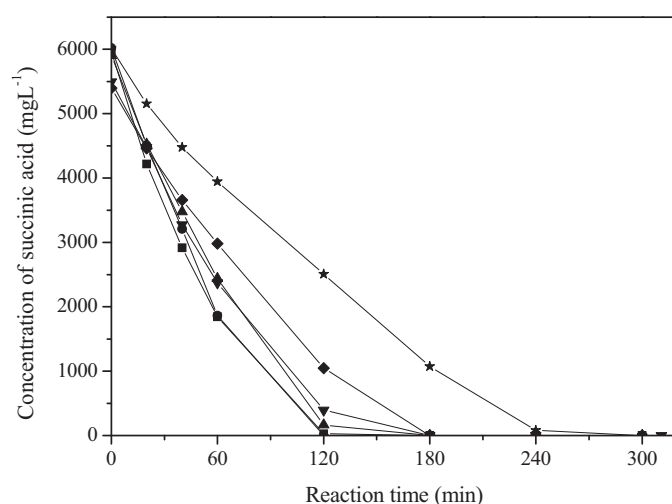


**Fig. 5.** CWAO of succinic acid (5 g L$^{-1}$) over the 0.5 wt% $Ru/Ce_xZr_{1-x}O_2$ catalysts (0.5 g catalyst) at 190°C under 50 bar total pressure. Influence of the support composition [x = 1 (■); 0.9 (●); 0.75 (▲); 0.65 (▼); 0.5 (◆); 0.16 (★)].

**Table 4**
CWAO of succinic acid over 0.5 wt% $Ru/Ce_xZr_{1-x}O_2$ catalysts at 190 °C under 50 bar total pressure (5 g L$^{-1}$ succinic acid, 0.5 g catalyst).

| Samples[*] | Ru loading[**] (%) | Initial reaction rate ($mol_{acid}$ h$^{-1}$ $mol_{Ru}^{-1}$)[***] | Succinic acid conversion after 40 min reaction (%) | TOC abatement after 40 min reaction (%) | Succinic acid conversion after 360 min reaction (%) | TOC abatement after 360 min reaction (%) | Ce leaching (mg L$^{-1}$) | Carbon adsorbed on the catalyst (wt%) |
|---|---|---|---|---|---|---|---|---|
| $Ru/CeO_2$ | 0.60 | 195 | 51 | 36 | 100 | 89 | 0.30 | 0.6 |
| $Ru/Ce_{0.9}Zr_{0.1}O_2$ | 0.60 | 177 | 47 | 44 | 100 | 93 | 0.50 | 0.6 |
| $Ru/Ce_{0.75}Zr_{0.25}O_2$ | 0.56 | 167 | 41 | 29 | 100 | 89 | 0.40 | 0.6 |
| $Ru/Ce_{0.65}Zr_{0.35}O_2$ | 0.52 | 165 | 40 | 28 | 100 | 85 | 0.70 | 0.5 |
| $Ru/Ce_{0.5}Zr_{0.5}O_2$ | 0.54 | 133 | 32 | 22 | 100 | 82 | 0.70 | 0.5 |
| $Ru/Ce_{0.16}Zr_{0.84}O_2$ | 0.34 | 118 | 26 | 18 | 100 | 76 | 0.96 | 2.9 |

[*] Atomic composition.
[**] Determined by ICP-OES.
[***] Calculated from the data acquired within the first 40 min of reaction.

the Pt ones confirmed the better activity of Ru at breaking C—C bonds [25].

As reported above for the Pt-based catalysts, the catalytic performances of the Ru catalysts also appeared to be affected by the Ce content in the $Ce_xZr_{1-x}O_2$ supports (Table 4). For example, the initial reaction rate increased from 118 to 195 $mol_{acid}$ h$^{-1}$ $mol_{Ru}^{-1}$ as the Ce content in the $Ce_xZr_{1-x}O_2$ support increased from 16 to 100 at.%.

Similarly, the TOC abatement was higher in the case of the Ru-based catalysts and ca. 90% mineralization was achieved after 360 min reaction. Acetic and acrylic acids were the only reaction products detected in the aqueous phase. Acetic acid was the most refractory towards further oxidation. However, compared to the Pt catalysts, the Ru catalysts were a little more active in the subsequent oxidation and mineralization of acetic acid since Ru demonstrated better performances at breaking C–C bonds, as already mentioned above.

Furthermore, no Ru or Zr leaching was ever detected in the effluent, and only Ce leaching was observed in the aqueous solution. However, very limited amounts (< 1 ppm) were analysed at the end of the reaction compared to the total amount of cerium in the catalyst and the $Ru/Ce_xZr_{1-x}O_2$ catalysts could still be considered to be stable under the applied reaction conditions.

In comparison with the best performing ruthenium-based catalysts developed by Perkas et al. [25], the 0.5 wt% $Ru/Ce_xZr_{1-x}O_2$ catalysts were observed to be ca. seven times more active, although their specific surface area of the $Ce_xZr_{1-x}O_2$ mixed oxides was significantly lower than that of the mesoporous supports used by Perkas et al. These results further confirmed the promoting effect of the $Ce_xZr_{1-x}O_2$ mixed oxides on the catalytic performances of the Ru catalysts in the CWAO of succinic acid.

The promoting effect of the $Ce_xZr_{1-x}O_2$ mixed oxides on the activity of metal-supported catalysts has to be related to their outstanding ability of activating oxygen to store and release oxygen under oxygen-rich and oxygen-poor conditions, respectively. This specific property to the $Ce_xZr_{1-x}O_2$ mixed oxides has been shown to be beneficial in terms of catalytic performances in many different reactions, whenever a redox mechanism is involved and the activation of oxygen is a key issue [20,24]. At the industrial scale, the main application is probably in the field of automotive pollution control (three-way catalysis).

Compared with other metal oxides ($TiO_2$, $ZrO_2$, $Al_2O_3$, $SiO_2$), the $Ce_xZr_{1-x}O_2$ mixed oxides may contain a high concentration of oxygen vacancies. These vacancies are directly involved in the oxygen activation process at the catalyst surface, leading to the formation of highly reactive oxygen species such as superoxides and peroxides.

In the CWAO reaction, the activation of oxygen was demonstrated to be a rate-determining step. From a mechanistic point of view, it has been shown in numerous studies that the reaction was (1) zero order with respect to the molecule to be oxidized (the molecule is strongly adsorbed and the catalyst surface is saturated) and (2) first order with respect to the oxygen (the oxygen activation is limiting). As such, any attempt to promote the adsorption/activation of the oxygen molecule dissolved in the aqueous phase and the formation of highly reactive oxygen species at the active sites was shown to have a direct impact on the catalyst performances in the CWAO reaction [9,18,23,24]. When $Ce_xZr_{1-x}O_2$ mixed oxides are used, oxygen vacancies would help the activation of oxygen from the liquid phase up to the active sites. In other words, the mixed oxides could offer an extra pathway for the activation of oxygen on the catalyst surface, in addition to the conventional activation route at the metal particle surface. This oxygen activation pathway would not be competing anymore with the adsorption of organic pollutants at the metal particle.

### 3.5. Stability of the 0.5 wt% $Ru/Ce_xZr_{1-x}O_2$ catalysts in the CWAO of succinic acid

Among the most active catalysts, the 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ catalyst was selected and the stability of this catalyst in the CWAO of succinic acid at 190 °C under 50 bar total pressure was investigated upon successive runs (recycling) in a batch reactor.

To start with, the stability of the bare $Ce_{0.9}Zr_{0.1}O_2$ support was tested. The evolution of the succinic acid concentration as a function of time upon recycling reactions is shown in Fig. 6. The $Ce_{0.9}Zr_{0.1}O_2$ support maintained good performances upon successive tests in the CWAO of succinic acid and ca. 100% succinic acid conversion was achieved after 360 min reaction in all cases. However, a slight
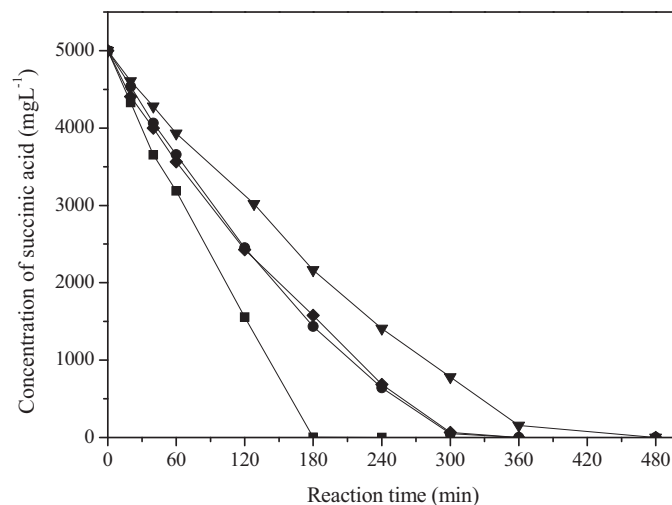


**Fig. 6.** CWAO of succinic acid (5 g L$^{-1}$) over the bare $Ce_{0.9}Zr_{0.1}O_2$ support (0.5 g) upon successive reactions (recycling tests) at 190 °C under 50 bar total pressure [fresh catalyst (■); first recycling (●); second recycling (▲); after first test and calcination under flowing air (60 L h$^{-1}$) at 500 °C for 4 h (♦)].

**Table 5**
CWAO of succinic acid over $Ce_{0.9}Zr_{0.1}O_2$ support at 190°C under 50 bar total pressure. Impact of the recycling (5 g L$^{-1}$ succinic acid, 0.5 g catalyst).

| Samples[*] | Run | Initial reaction rate (mmol$_{acid}$ h$^{-1}$ g$_{cat}$$^{-1}$)[**] | Succinic acid conversion after 40 min reaction (%) | TOC abatement after 40 min reaction (%) | Carbon adsorbed on the oxide (wt%) |
|---|---|---|---|---|---|
| $Ce_{0.9}Zr_{0.1}O_2$ | Fresh | 4.1 | 27 | 25 | 1.0 |
| | First recycling | 3.9 | 20 | 15 | 1.0 |
| | Second recycling | 3.2 | 14 | 10 | 1.0 |
| | After reaction and calcination | 3.5 | 19 | 11 | 1.0 |

[*] Atomic composition.
[**] Calculated from the data acquired within the first 40 min of reaction.

deactivation was observed and the initial succinic acid degradation rate gradually decreased from 4.1, 3.9 to 3.2 mmol$_{acid}$ h$^{-1}$ g$_{cat}$$^{-1}$ for the fresh $Ce_{0.9}Zr_{0.1}O_2$ sample and after one and two recycling runs, respectively (Table 5). Upon CWAO of organic compounds, the deactivation of heterogeneous catalysts was quite frequently observed. Depending on the nature of the catalyst, the oxidized pollutant and the operating conditions, the deactivation was shown to originate from (1) the leaching of active phases in the hot acidic reaction medium; (2) the strong adsorption of carbonaceous compounds on the catalyst surface; (3) the collapse of the active surface (surface area) under hydrothermal conditions; (4) the oxidation of the active phase upon reaction or (5) the decrease of the active phase accessibility (sintering, encapsulation, etc.) [10–12]. In our case, no leaching was ever detected by ICP-OES even after repeated cycles (below detection limit), indicating that the $Ce_{0.9}Zr_{0.1}O_2$ support was chemically stable under the applied reaction conditions. Similarly, no significant evolution of the specific surface area of the oxide was evidenced. Furthermore, the amount of carbon deposited on the oxide surface appeared to be quite limited, stayed constant ca. 1 wt% whatever the number of runs, and no significant change was observed in the infrared spectra (not shown). However, to get deeper insights on the possible impact of the carbonaceous deposit on the activity, the $Ce_{0.9}Zr_{0.1}O_2$ oxide was tested one time, filtrated, dried and calcined under flowing air (60 L h$^{-1}$) at 500°C for 4 h. After burning the carbonaceous deposit, the mixed oxide was evaluated again in the CWAO of succinic acid. By comparison with the untreated sample (first recycling), no improvement was observed and it could be concluded that carbonaceous deposits are not directly responsible for the deactivation. In conclusion, some modification of the active sites on the oxide surface (redox properties) was probably responsible for the deactivation.

In a second time, the stability of the 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ catalyst was evaluated (Fig. 7). The catalyst still exhibited very good performances even after three runs, but a progressive deactivation was evidenced, and 100% conversion of succinic acid was obtained after 120, 300 and 360 min reaction for the fresh catalyst and after one and two recycling, respectively. In the meantime, the initial reaction rate obviously decreased from 177 to 52 mol$_{acid}$ h$^{-1}$ mol$_{Ru}$$^{-1}$ (Table 6). The main deactivation process occurred upon the first test using the fresh sample. Since no Ru leaching was detected, no major evolution of the specific surface area was observed and no significant influence of the carbonaceous deposit was evidenced, some modifications of the physical and/or chemical properties of the active phase (dispersion, oxidation state, etc.) are probably involved in the deactivation of the 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ catalyst.

In summary, the deactivation of the $Ce_{0.9}Zr_{0.1}O_2$ support and the 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ catalyst could not be explained by the leaching of the active phase, the adsorption of carbonaceous deposits on the catalyst surface or the decrease of the specific surface area. However, some changes in the surface properties of the solids and the chemical state of the active phase, especially modifications in the O/Ce and/or O/Ru surface ratios could play a major role in the deactivation. Such modifications would hinder the activation of the oxygen on the catalyst surface and slow down the CWAO reaction.

### 3.6. Insights into the kinetics of the CWAO of succinic acid over 0.5 wt% $Ru/Ce_xZr_{1-x}O_2$

The CWAO reaction is an activated process and the reaction temperature was repeatedly reported to have a major impact on the removal of organic compounds [23,24]. Fig. 8 shows the effect of the reaction temperature on the CWAO of succinic acid over 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ in the range of 150–190°C. As expected,
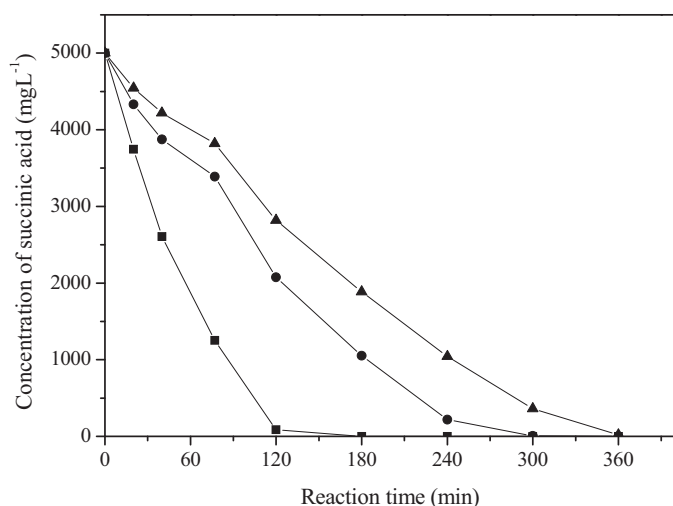
**Fig. 7.** CWAO of succinic acid (5 g L$^{-1}$) over the 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ catalyst (0.5 g catalyst) upon successive reactions (recycling tests) at 190°C under 50 bar total pressure [fresh catalyst (■); first recycling (●); second recycling (▲)].
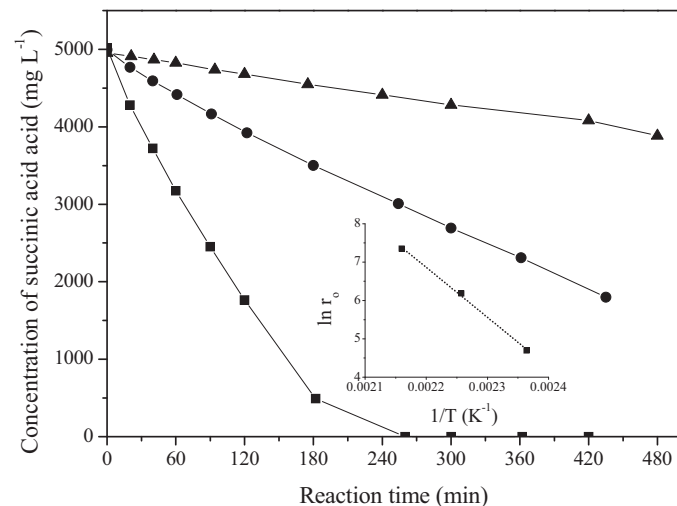
**Fig. 8.** CWAO of succinic acid (5 g L$^{-1}$) over the 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ catalyst (0.3 g) under 50 bar total pressure. Impact of the reaction temperature [190°C (■); 170°C (●); 150°C (▲)].

**Table 6**
CWAO of succinic acid over 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ catalyst at 190°C under 50 bar total pressure. Impact of the recycling (5 g L$^{-1}$ succinic acid, 0.5 g catalyst).

| Samples[*] | Run | Reaction rate ($mol_{acid}$ h$^{-1}$ $mol_{Ru}$$^{-1}$)[**] | Succinic acid conversion after 40 min reaction (%) | TOC abatement after 40 min reaction (%) | Carbon adsorbed on the catalyst (wt%) |
|---|---|---|---|---|---|
| 0.5wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ | Fresh | 177 | 47 | 44 | 0.6 |
| | First recycling | 78 | 23 | 23 | 1.0 |
| | Second recycling | 52 | 16 | 11 | 1.0 |

[*] Atomic composition.
[**] Calculated from the data acquired within the first 40 min of reaction.

the initial succinic acid degradation rate increased from 11 to 157 $mol_{acid}$ h$^{-1}$ $mol_{Ru}$$^{-1}$, and the succinic acid conversion reached ca. 18, 62 and 100% after 420 min reaction as the temperature increased from 150 to 190°C. From the Arrhenius plot, the activation energy for the CWAO of succinic acid over the 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ catalyst was calculated to be ca. 108 kJ mol$^{-1}$. This value was lower but quite similar to the activation energy measured with a 2.8 wt% $Ru/TiO_2$ catalyst (ca. 125 kJ mol$^{-1}$) [26] and confirmed the excellent performances of 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ as a catalyst in the degradation of succinic acid via CWAO.

In order to determine the reaction orders with respect to the reactants and establish a simplified rate law, the effect of the initial concentration of succinic acid (1–5 g L$^{-1}$) on the performances of the 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ catalyst at 170°C under 50 bar total pressure was investigated (Fig. 9). Although succinic acid was eliminated faster from the aqueous solution as the initial concentration decreased, the initial reaction rate was only slightly influenced and varied from 39, 45 to 49 $mol_{acid}$ h$^{-1}$ $mol_{Ru}$$^{-1}$, as the concentration in succinic acid increased from 1, 2 to 5 g L$^{-1}$, respectively. The reaction order with respect to succinic acid was deduced to be ca. 0.1. Similarly, the influence of the oxygen partial pressure on the CWAO of succinic acid over 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ at 170°C under 50 bar total pressure was investigated (Fig. 10). For that purpose either synthetic air (20 vol.% $O_2$ in $N_2$) or pure oxygen was used. The corresponding oxygen partial pressure was 9 and 29 bar, i.e. ca. 0.3 and 1.0 g L$^{-1}$ of oxygen dissolved in the aqueous phase, respectively. When substituting air for pure oxygen, the succinic acid conversion at a given reaction time and the initial reaction rate increased. For example, the conversion increased from 29 to 44% after 180 min reaction and the initial reaction rate increased from 49 to 76 $mol_{acid}$ h$^{-1}$ $mol_{Ru}$$^{-1}$ as the oxygen partial pressure increased from 9 to 29 bar. The reaction order



**Fig. 10.** CWAO of succinic acid (5 g L$^{-1}$) over the 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ catalyst (0.3 g) at 170°C under 50 bar total pressure. Impact of the initial oxygen partial pressure using either synthetic air (●) or pure oxygen (■).

with respect to oxygen was calculated to be ca. 0.4. As a result, a simplified rate law for the CWAO of succinic acid over 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ catalyst could be proposed as follows:

$$r = k[\text{succinic acid}]^{0.1}[\text{oxygen}]^{0.4}.$$

This rate law appeared to be significantly different from what was usually described for the CWAO of organic compounds over noble-metal-based catalysts supported on simple oxides such as titanium or zirconium oxides. Although many different values have been reported in the literature for the reaction order with respect to oxygen, in the range 0–1.4 [13,17,26–38], the oxygen activation step was very often reported to be rate limiting. It was reported for example that the CWAO of 2-chlorophenol over $Ru/ZrO_2$ catalyst was zero order with respect to the organic compound and first order with respect to oxygen [17]. Schematically, the catalyst surface is saturated with the pollutant and the oxygen access to the active site is a limiting step for the overall conversion of organics. In the present case, when the $Ce_xZr_{1-x}O_2$ mixed oxides were involved, the reaction order with respect to succinic acid was still close to zero, indicating that the surface was nearly saturated with succinic acid but the reaction order with respect to oxygen was much lower than 1. This result indicated that the accessibility of oxygen to the active sites was significantly easier in the presence of the $Ce_xZr_{1-x}O_2$ supports. This observation further confirmed the existence of an additional pathway for the activation of oxygen on the catalyst surface, independently on the adsorption/activation sites which were demonstrated to be saturated by succinic acid.

## 4. Conclusions

$Ce_xZr_{1-x}O_2$ mixed oxide supports, 0.5 wt% $Pt/Ce_xZr_{1-x}O_2$ and 0.5 wt% $Ru/Ce_xZr_{1-x}O_2$ catalysts were evaluated in the CWAO of
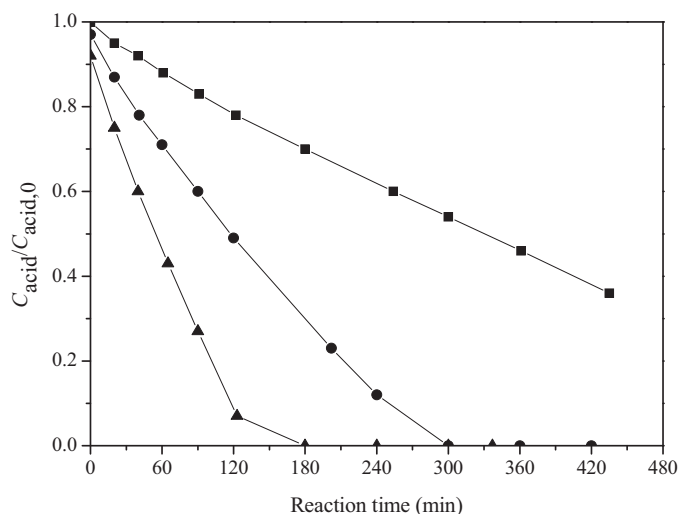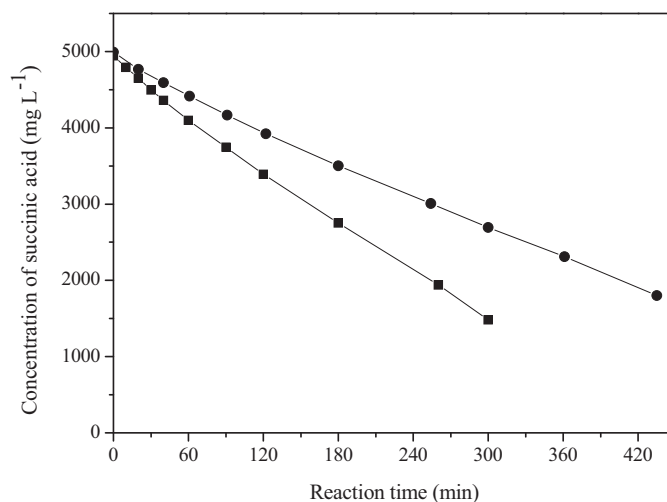


**Fig. 9.** CWAO of succinic acid over the 0.5 wt% $Ru/Ce_{0.9}Zr_{0.1}O_2$ catalyst (0.3 g) at 170°C under 50 bar total pressure. Impact of the initial succinic acid concentration [5 g L$^{-1}$ (■); 2 g L$^{-1}$ (●); 1 g L$^{-1}$ (▲)].

succinic acid at 190°C under 50 bar total pressure (ca. 7 bar oxygen partial pressure, i.e. 0.3 $g_{O2}$ $L^{-1}$ in the aqueous phase). Both the bare mixed oxides and the supported Pt- and Ru-based catalysts demonstrated good performances in the CWAO of succinic acid under the applied reaction conditions. A direct connexion was observed between the activity and the Ce content in the $Ce_xZr_{1-x}O_2$ mixed oxide, i.e. the redox properties of the support. The higher the Ce content, the higher the succinic acid removal rate and the better the mineralization. Upon recycling, deactivation of the catalysts was noticed. It could be tentatively related to some modifications in the surface properties of the solids and the chemical state of the active phase. Finally, the reaction was observed to be almost zero order with respect to succinic acid (+0.1) but +0.4 order with respect to oxygen, indicating the existence of an additional pathway for the activation of oxygen on the catalyst surface which is not competing anymore with succinic acid.

## Acknowledgments

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